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Research Article

Direct Synthesis of Porous Multilayer Graphene Materials Using Thermal Plasma at Low Pressure

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Porous multilayer graphenes have been synthesized by decomposition of hydrocarbons in a thermal plasma jet. Products of synthesis were characterized by electron microscopy, thermogravimetry, Raman spectroscopy, and X-ray diffraction. Possibility of producing a wide range of graphene materials with different morphology and structure has been shown. Influence of the experimental conditions on mesopores structure of the synthesis products has been investigated using the method of "limited evaporation."

1. Introduction

Surface area and porosity of the catalyst are essential for catalysis. The existence of macropores, mesopores, and micropores on the surface of solids affects their adsorption, diffusion, and capillary and mechanical properties depending on the porosity and determines the specifics of particular adsorptive and catalytic processes. According to the IUPAC classification macropores are pores with average diameter greater than 500 Å; micropores refer to pores with diameter less than 20 Å, and mesopores are pores of intermediate size from 20 to 500 Å. Mesoporous structures are characterized by the availability of functional groups to participate in the formation of supramolecular structures as well as the ability to vary and control functionality and pore geometry. Mesoporous carbon materials with a developed porous structure are widely used as the basis of catalysts and adsorbents.

Conventional production methods of carbon material, physical and chemical activation, do not allow reliable control over textural properties of the resultant materials if it is necessary to obtain a mesoporous carbon. Relatively recently developed template method of synthesis using mesoporous silica allows producing materials with required pore size and ordered structure. However, this method has several disadvantages, such as multistage, use of a large amount of expensive and corrosive chemicals, and large amount of liquid waste [1].

Our purpose was to study the possibility of obtaining mesoporous graphene nanomaterials by decomposition of hydrocarbons in a plasma jet reactor, so that those nanomaterials on one hand would have a developed specific surface and on the other hand a minimal share of micropores, the presence of which in the catalyst, as known, is not desirable. Interest in mesoporous graphenes is due to its use not only in catalysts but also in supercapacitors, in lithium-air battery, and in membranes for gas separation [2–4].

It is important to solve the problem of large-scale production of graphene. From this point of view the application of the thermal plasma when the plasma torches are used is very interesting. Using plasma jet reactor based on the DC plasma torch pure layered graphene was produced [5]. The number of layers of graphene sheets was controlled by controlling the rate of ethanol injection.

Our experiment involved a simultaneous input of hydrocarbons with the working gas (helium and argon) into a plasma torch with power up to 40 kW, wherein heating and

Table 1: Technological conditions.

Power (kW)	Current (A)	Voltage (V)	Gas pressure (Torr)	Helium flow rate (g/s)	Argon flow rate (g/s)	Propane-butane flow rate (g/s)	Methane flow rate (g/s)	Acetylene flow rate (g/s)
30–40	350–400	60–110	150–730	0.5–0.9	3.0–3.75	0.11–0.30	0.15–0.37	0.05–0.16

decompositions occurred in the plasma jet and in the region of the arc discharge, followed by cooling carbon vapor and condensation of the synthesis product on metallic surfaces.

The novelty of our work is associated with a significant increase in the rate of production of carbon vapor in comparison with study [5]. In addition, we used as a carbon source gases with different ratios of carbon and hydrogen in their composition: propane-butane, methane, and acetylene. It is well known that hydrogen plays a critical role in graphene synthesis [6]. We first investigated the synthesis process at different gas pressures in the reactor. The porous structure of the graphene materials synthesized by use of the thermal plasma jet has not been investigated earlier.

2. Experimental Procedures

For the synthesis of graphene materials thermal plasma generator was used which is a high current divergent anode-channel DC plasma torch. A detailed description of the experimental setup was given in the studies [7, 8]. The experiment involved a simultaneous input of hydrocarbons or soot with the plasma forming gas into the plasma torch, wherein heating and decompositions occurred in the plasma jet and in the region of the arc discharge, followed by condensation of the synthesis product on metallic surfaces. Consumption of carbon, plasma forming gas, and plasma torch power were changed independently of each other. For the experimental conditions the electric power of plasma torch was set up to 40 kW. Helium and argon were used as plasma forming gases.

For each experiment, the input of hydrocarbons was carried out after establishment of the temperature field in a graphite reactor (determined by temperature of water in the cooling system) and the establishment of the electrical characteristics of the plasma torch. The current value of the plasma torch was constant during the experiment and equaled 350 A for argon and 400 A for helium. Arc voltage was changed from 60 to 110 V depending on gas pressure and gas flow rate.

Methane, acetylene, and a mixture of propane-butane in the ratio 30 : 70% were used as the source of carbon. Decomposition of hydrocarbons in plasma jet reactor was carried out using helium and argon as a working gas. Their flow rate varied from 0.5 to 3.75 g/s. Experiments were conducted at various pressures and flow rates of hydrocarbons. The pressure varied from 150 to 730 Torr, and hydrocarbon flow rate varied from 0.05 to 0.37 g/s. The time duration of the experiments was 10–20 minutes. The experimental conditions are presented in Table 1.

Method of electron microscopy was used to investigate the structure of the synthesized products on a scanning electron microscope of MIRA 3 TESCAN with Schottky field emission cathode in high vacuum regime. Raman spectra were investigated by using the exciting radiation at a wavelength of 532 nm (NTEGRA spectrum). X-ray diffraction data were obtained at room temperature on a powder diffractometer Stoe Stadi P. To determine the characteristics of the porous structure (pore volume, pore radius, and surface area) we used a relatively new method of adsorption, "limited evaporation" [9, 10], based on the analysis of the kinetics of evaporation of the adsorbate from the test material. To evaluate the specific surface area of materials the classic BET method was applied using a low-temperature nitrogen adsorption analyzer Quadrasorb SI. Efficiency of the synthesis and thermal stability and phase composition of carbon products were evaluated by thermogravimetry and differential scanning calorimetry on a synchronous thermal analyzer STA 409PC Luxx (NETZSCH) with linear heating sample in air at the rate of 10 K/min at temperatures up to 1000°C.

3. Results

The experiments on decomposition of propane-butane mixture show that the highest yield of graphene materials is obtained under the following conditions: plasma forming gas is helium, pressure is 710 Torr, and flow rate of the hydrocarbon is 0.23 g/s. Under these conditions, the amount of amorphous carbon is 4 wt.% and the proportion of graphitized particles is less than 2 wt.%. This conclusion is based on the thermogravimetric analysis of the synthesized carbon structures. Figure 1 presents results of thermogravimetric analyses of synthesis products produced by decomposition of propane-butane at these conditions.

Depending on the type of plasma gas, pressure and flow rate of plasma gas, and flow rate of propane-butane mixture, morphology of the synthesis products varies from crumpled structure to large flakes with a transverse dimension of 600 nm. For example, crumpled structures were synthesized at pressures of 350–710 Torr using a flow of argon of 3.5–3.75 g/s and at pressure of 710 Torr and 350 Torr with the use of helium with a flow rate of 0.75 and 0.95 g/s, respectively. Large flakes having transverse dimensions of 600 nm were synthesized at pressure of 350 Torr of helium at a rate of 0.75 g/s. Figure 2 shows the example of SEM image of products of synthesis.

Specific surface area of the samples with a transverse dimension of 300–600 nm was 350–400 m^2/g using the BET method. The main range of the pore radius is in the range of 100–400 Å, corresponding to mesopores. Figure 3 presents the comparison of pore size distribution for two gas pressures used in the experiment.

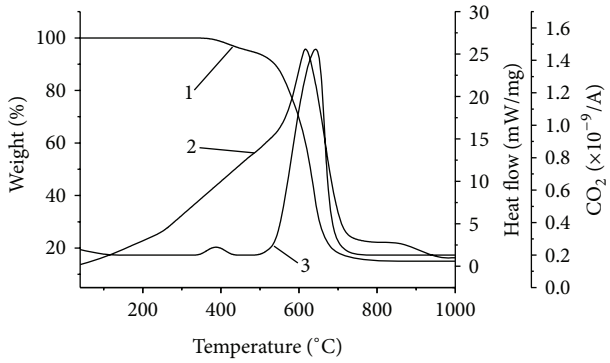

FIGURE 1: Results of thermogravimetric analyses of synthesis products produced by decomposition of propane-butane at a pressure of 710 Torr. Plasma forming gas is helium. (1) Loss of weight, (2) heat flow, and (3) rate of generation of CO_2.

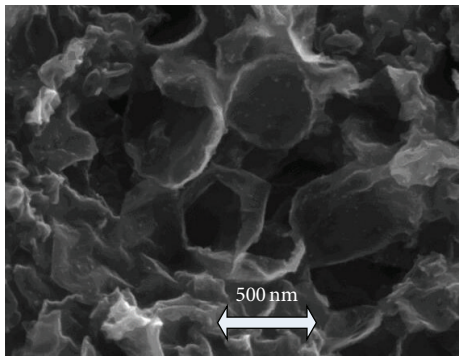

FIGURE 2: Morphology of synthesis products from the decomposition of propane-butane at a pressure of 710 Torr.

Figure 4 shows a typical XRD spectrum of the sample with the graphene structures, characteristic of all products produced from the decomposition of propane-butane. The diffractogram of the sample is composed of two intense halos. The strongest reflex is at the angle 44.20°. This is offset reflection Fe (111) from the bottom of the steel cell. Less intense peak corresponds to a phase of graphite. Reflexes of graphite are 26.63° and 43.49°. Data on the XRD spectra confirm indirectly the synthesis of graphene materials.

According to SEM images and thermogravimetry of the synthesis products from methane with the use of helium at pressure of 350 Torr and flow rate of 0.75 g/s, 65 wt.% graphene structures are formed which are oxidized in the temperature range typical for carbon nanotubes. The transverse dimension is in the range from 400 to 600 nm. By increasing the pressure of helium and argon to 500 Torr in experiments with methane, the size of graphene structure at the target increases. When the pressure is decreased to 150 Torr, the concentration of graphite and amorphous phase of carbon increases. Figure 5 presents the morphology of synthesis products from the decomposition of methane. Figure 6 shows the results of thermogravimetric analyses.

Thermogravimetric study of the phase composition of the synthesized products formed by the decomposition of

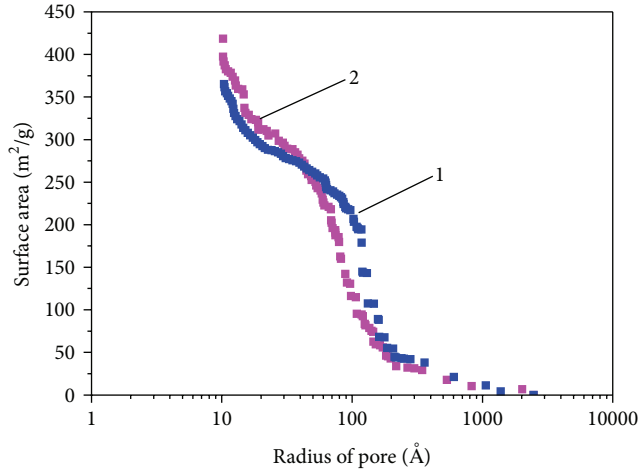

FIGURE 3: Specific surface area as a function of the pore radius for the samples synthesized using helium at a pressure of 350 Torr (1) and 710 Torr (2). Carbon source is propane-butane.

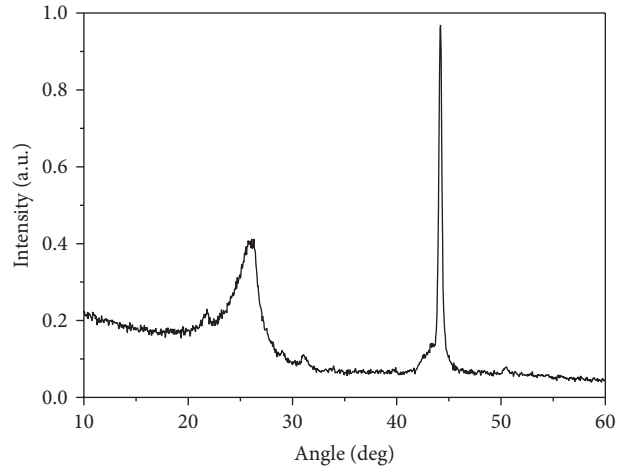

FIGURE 4: XRD spectrum of synthesized product using decomposition of propane-butane at 350 Torr.

methane, propane-butane, and acetylene has shown the narrowest temperature range in which the loss of weight corresponds to methane. The weight change of the samples produced by the decomposition of methane is accompanied by an exothermic peak in a heat flow curve. For other gases 2-3 peaks have been observed correlated with anomalies in the form of "steps" on the curves of the loss of weight. When comparing forms of the heat flow peaks for different samples synthesized from different hydrocarbons it was found that the narrowest and highest peak is observed for the samples that were produced from methane. Thus, the most structurally homogeneous sample was produced by decomposition of methane.

In the Raman spectra of the investigated samples (untreated) features characteristic of graphene materials were observed [11, 12]. The spectra were obtained from the surface of the samples at several points in the range from 100 to 3000 cm^{-1}. Figure 7 presents a typical Raman spectrum

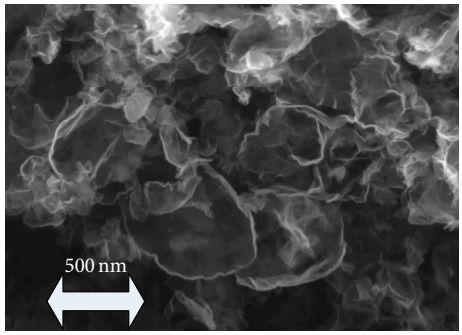

Figure 5: Morphology of synthesis products from decomposition of methane at a pressure of 350 Torr.

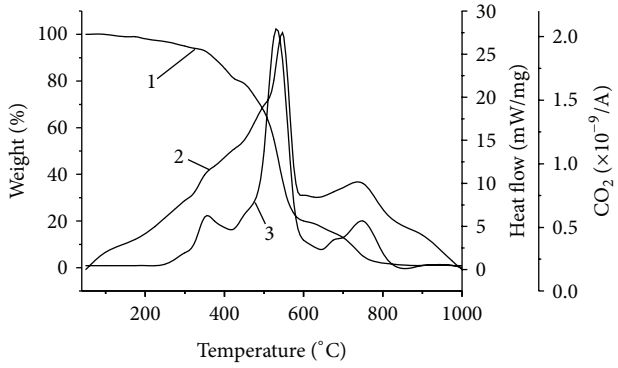

Figure 6: Results of thermogravimetric analyses of synthesis products produced by decomposition of methane at a pressure of 710 Torr. Plasma forming gas is helium. (1) Loss of weight, (2) heat flow, and (3) rate of generation of CO_2.

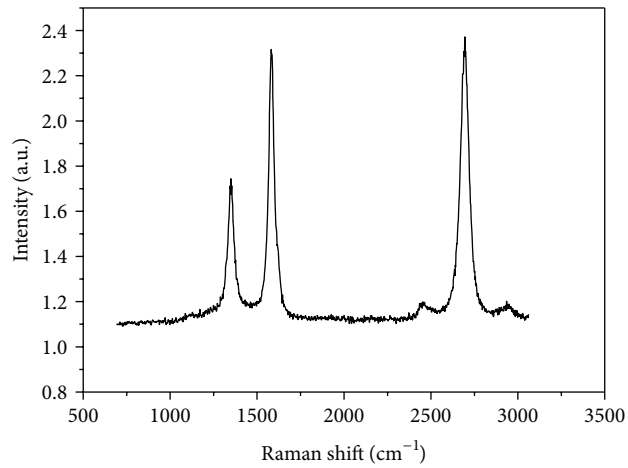

Figure 7: Raman spectrum of the sample from decomposition of methane.

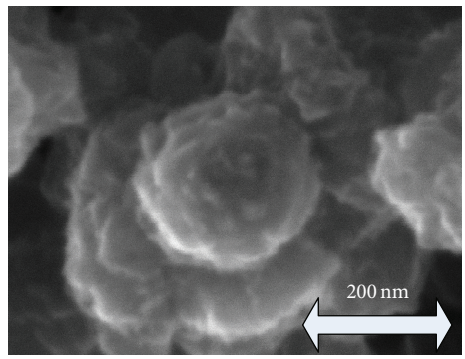

Figure 8: Morphology of synthesis products from the decomposition of acetylene at a pressure of 150 Torr. Helium flow rate is 0.75 g/sec and acetylene flow rate is 0.11 g/s.

of graphene materials produced by the decomposition of methane. The three intense features are the D band at 1349 cm^{-1}, the G band at 1584 cm^{-1}, and 2D band at 2693 cm^{-1}. It was concluded that the synthesized graphene flakes had a number of layers which were less than five. Some flakes of graphene materials were monolayer. The number of the graphene layers can be estimated from the 2D peak position and peak intensity G. The intensity of the G line was considered in relation to the intensity of the 2D line. Depending on the relationship of intensities I_{2D}/I_G the number of layers in our samples has been estimated. Samples had nonuniformity surface and their parameters varied within certain limits. Thus, the spectra taken from different areas of one sample may differ. Therefore, there is a range of layers. Our results agree with results of the work [13]. According to this work the position of 2D line changes before achieving 10 graphene layers. After that, the position of the line does not change and corresponds to the highly oriented pyrolytic graphite. In our conditions, the samples have less than 10 layers, with the largest shift D line observed at smaller number of layers. The majority of our samples had 2–5 graphene layers. In our study we used the well-known approach to make conclusions about the presence of graphene materials and about the number of layers of graphene structures in accordance with the work [13].

The maximum yield of crumpled structures of graphene materials with openwork boundaries is observed by using argon at a pressure of 650–670 Torr and a flow rate of methane equal to 0.37 g/s. Specific surface area determined by BET method in the case of methane is slightly higher than when using propane-butane and is 400 m^2/g. The maximum yield of graphene materials in the synthesis products was 91% and was achieved at a pressure of 500 Torr.

Upon decomposition of acetylene using argon and helium plasma, crumpled graphene structure was produced at pressure range from 150 to 350 Torr. Flow rate of acetylene was from 0.05 to 0.16 g/s. Using helium at its flow rate of 3.6 g/s apart from graphenes formation, formation of carbon fibers was observed which corresponded to the presence in the thermogram of a less intense peak in the temperature range 370–570°C. Figure 8 shows the SEM image of products of synthesis when acetylene was used. Figure 9 presents results of thermogravimetric analyses for this case.

On the whole, Raman spectra and TGA curves have been obtained for 133 samples of synthesized carbon nanomaterials. Phase composition of synthesized carbon nanostructures varied widely depending on the conditions of decomposition

Table 2: The range of concentrations of synthesized carbon nanostructures.

Amorphous carbon (weight %)	Graphenes (weight %)	Graphitized particles (weight %)
4.27–12.49	55.64–94.59	0.77–9.33

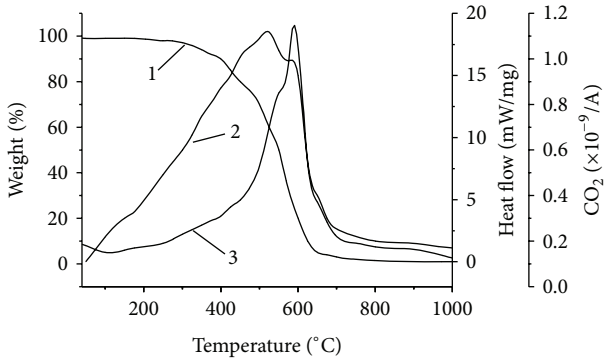

Figure 9: Results of thermogravimetric analyses of synthesis products produced by decomposition of acetylene. (1) Loss of weight, (2) heat flow, and (3) rate of generation of CO_2.

of the hydrocarbons. Table 2 shows the concentration range of the amorphous carbon, graphenes, and the graphitized particles.

Comparative studies were conducted on the porosity of the samples produced by decomposition of propane-butane, methane, and acetylene, with the use of the limited evaporation method, which is based on the analysis of the kinetics of evaporation of the adsorbate from tested material. The range of measured relative pressures varied from 0.995 to 0.01 and pore radii change from 10 to 3000 Å.

Figures 10 and 11 show the structural features of the synthesized graphene materials porous structure. Curves of the pore size distribution correspond to typical meso-macroporous samples. The base diameter for samples 1 and 2 ranges from 100 to 400 Å and the total pore volume in this range for sample 1 is 2.1 cm^3/g and for sample 2 is 1.8 cm^3/g. For sample 3 main pore diameter was 200 to 800 Å and pore volume 2.2 cm^3/g.

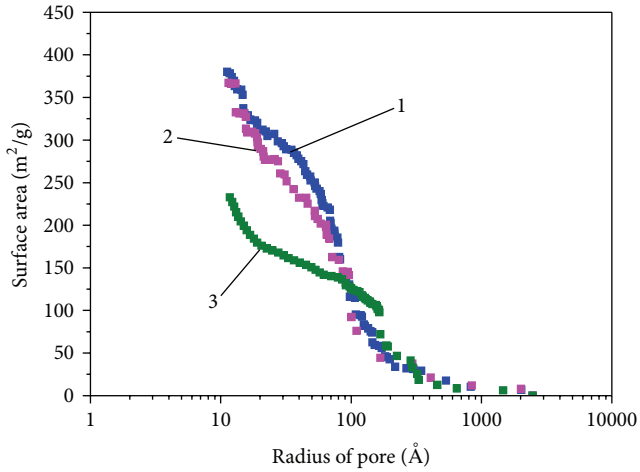

Figure 10: Specific surface area as a function of the pore radius. (1) Pressure is 710 Torr, plasma gas is helium, and carbon source is propane-butane. (2) Pressure is 710 Torr, plasma gas is helium, and carbon source is methane. (3) Pressure is 350 Torr, plasma gas is helium, and carbon source is acetylene.

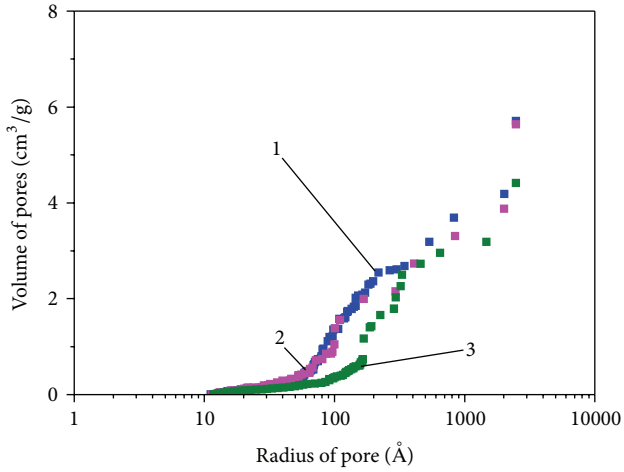

Figure 11: Volume of pore as a function of the pore radius. (1) Pressure is 710 Torr, plasma gas is helium, and carbon source is propane-butane. (2) Pressure is 710 Torr, plasma gas is helium, and carbon source is methane. (3) Pressure is 350 Torr, plasma gas is helium, and carbon source is acetylene.

4. Conclusions

It is shown that, by using a plasma jet synthesis technology, multilayered graphene materials may be formed at low pressures without the presence of catalysts. Morphology and structural properties of the materials depend on carbon source flow rate and the gas pressure. The measurements show that the graphenes produced by decomposition of methane have better structural perfection than those synthesized from a mixture of propane-butane and acetylene. These materials are composed of polycrystalline graphene flakes with a highly developed porous structure formed mainly of macro- and mesopores with different diameters. The correlation between the conditions of synthesis and specific surface area of graphene materials has been determined. With increasing gas pressure, its value increases. The total volume and area pore depending on their radius have been found. These results showed that the synthesized carbon structures using the plasma jet are mesoporous. These mesoporous graphene materials are of interest for use in catalysts, in supercapacitors, and in the lithium-air batteries.

Specific surface area and pore system of synthesized graphenes are comparable with properties of materials used as carriers of catalytically active components, such as alumina, silica-alumina, and activated charcoal. Furthermore, according to the literature data graphenes have high chemical resistance and mechanical strength. Overall, the multilayer

graphene structures synthesized using plasma jet are attractive for new catalysts. The results suggest the possibility of scale production of graphene materials with predetermined texture.

Our results are in agreement with the results published in [5]. In this paper the conclusion was made that graphene materials of similar type were produced in plasma jet reactor when the same methods of diagnostics were used. The main difference of our work is that as the carbon source we used gases instead of liquid alcohol. It has allowed increasing the rate of formation of graphene materials hundreds of times.

Conflict of Interests

The authors Ravil Amirov, Marina Shavelkina, Nariman Alihanov, Evgeny Shkolnikov, Alexander Tyuftyaev, and Natalya Vorob'eva declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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